15:39:21 OCA PAD AMENDMENT - PROJECT HEADER INFORMATION 05/05/92

Active

Project #: E-27-659 Cost share #: Rev #: 1
Center # : 10/24-6-R7453-0A0 Center shr #: OCA file #:
Work type : RES
Contract#: CTS-9104585 Mod #: ADM REV Document : GRANT
Prime #: Contract entity: GTRC

Subprojects ? : N CFDA: 47.041
Main project #: PE #:

Project unit: TEXT ENGR Unit code: 02.010.130
Project director(s):
WARNER S B MAT ENGR (404)894-2852
POLK M B TEXT ENGR (404)-

Sponsor/division names: NATL SCIENCE FOUNDATION / GENERAL
Sponsor/division codes: 107 / 000

Award period: 920315 to 930831 (performance) 931130 (reports)

Sponsor amount	New this change	Total to date
Contract value	0.00	50,000.00
Funded	0.00	50,000.00
Cost sharing amount		0.00

Does subcontracting plan apply ?: N

Title: PHYSICS OF SOLID STATE POLYMERIZATION

PROJECT ADMINISTRATION DATA

OCA contact: Mildred S. Heyser 894-4820

Sponsor technical contact

MARIA BURKA
(202)357-9606

NATIONAL SCIENCE FOUNDATION
1800 G STREET, NW
WASHINGTON, DC 20550

Sponsor issuing office

MARIAN C. SCHEINER
(202)357-9626

NATIONAL SCIENCE FOUNDATION
1800 G STREET
WASHINGTON, D.C. 20550

Security class (U,C,S,TS) : U ONR resident rep. is ACO (Y/N): N
Defense priority rating : supplemental sheet
Equipment title vests with: Sponsor GIT X

Administrative comments -
TO CORRECT EFFECTIVE DATE AND PERFORMANCE ENDING DATE PER
FAX APPROVAL FROM MARIAN SCHEINER/NSF 5/5/92.

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

Closeout Notice Date 02/03/94

Project No. E-27-659 Center No. 10/24-6-R7453-0A0

Project Director WARNER S B School/Lab TEXT ENGR

Sponsor NATL SCIENCE FOUNDATION/GENERAL

Contract/Grant No. CTS-9104585 Contract Entity GTRC

Prime Contract No.

Title PHYSICS OF SOLID STATE POLYMERIZATION

Effective Completion Date 930831 (Performance) 931130 (Reports)

Closeout Actions Required:	Y/N	Date Submitted
Final Invoice or Copy of Final Invoice	N	
Final Report of Inventions and/or Subcontracts	N	
Government Property Inventory & Related Certificate	N	
Classified Material Certificate	N	
Release and Assignment	N	
Other	N	

CommentsLETTER OF CREDIT APPLIES. 98A FORM SATISFIES PATENT REQUIREMENT.

Subproject Under Main Project No.

Continues Project No.

Distribution Required:

Project Director	Y
Administrative Network Representative	Y
GTRI Accounting/Grants and Contracts	Y
Procurement/Supply Services	Y
Research Property Managment	Y
Research Security Services	N
Reports Coordinator (OCA)	Y
GTRC	Y
Project File	Y
Other CARL BAXTER-FMD	Y
	N

E-27-659
1

COPY

Maria Burka - CTS
National Science Foundation rm. 1115
1800 G St., N.W.
Washington, DC 20277

25 Sept. 1993

Dear Maria,

Enclosed is the paperwork for close-out of the ***Physics of Solid State Polymerization*** project. We have conducted some very good work on the subject and I am enclosing a manuscript that we have submitted to J. Poly. Sci. for publication. The work on the project was roughly divided into two parts. I worked with a student on physical and mechanical aspects of heat treatment. Dr. Polk worked with a student on chemical aspects of heat treatment, focusing largely on synthesis of monomers and polymers with labeled groups. The group labels in thermotropic copolyesters will allow direct and definitive determination of the important question - whether defects, that is, chain ends, are clustered in fibers or not. We have not published the results from Dr. Polk's work largely because it is not quite yet finished. The summary I have provided lets you know what step we have reached.

I will not describe the sort of work that I have completed, since you can simply read all or part of the article. The work was quite successful. It represents one of the first papers published on heat treatment of thermotropic polymers. A number of useful and important scientific facts were uncovered and are presented: the irreversibility of the increase in melting temperature, the superheating effect, the anisotropy of tenacity increases, the mobility analysis, the structural model, and so on. I will be presenting the work at the Fiber Society Fall Conference at Cornell University on Oct. 11. The work will also be presented at the SPE meeting in San Francisco in May 1994.

Please let us know whether you would entertain a larger multiyear proposal to continue this sort of work on thermotropic polymers. We would include other thermotropic polymers, expand our work on PET because we have an idea that may work, include heat treatment of acrylics, complete the work on NMR to obtain local environments for tagged end groups (i.e. analyze clustering directly), and so on. (We have recently added a new faculty member at GA Tech whose chief area of expertise is solid state NMR of polymers. He will be helping us complete the work.) Although we hope you do request us to submit a large proposal to continue this work, whether you do or not, we do thank you for sponsorship of the work we have completed.

Sincerely,

SB Warner
Associate Professor

PART II - SUMMARY OF COMPLETED PROJECT

The chief objective of the work ***Physics of Solid State Polymerization*** was to elucidate the reason for the significant increase in tenacity of thermotropic copolyester fibers upon heat treatment, which are conditions that promote both annealing and solid state polymerization. As reported by a number of authors, annealing causes the crystals to perfect. The increase in melting temperature and tenacity of thermotropic copolyester Vectran® is due to the increase in molecular length. Such effects are not observed in poly(ethylene terephthalate) because the molecules are not essentially straight in fibers. The increase in molecular occurs by chain extension in the solid state, but the chemistry of the processes differ from those used to melt synthesize the polymer. For example, according to gas phase infrared spectroscopy, the major byproduct of solid state polymerization are carbon dioxide and water, and not acetic acid. Diffusion analysis suggests the polymer chain ends are rather mobile at heat treatment temperatures, suggesting that chain ends have sufficient time to diffuse into proximity to react. A new diffusive transport mechanism based on transesterification is also suggested. The structure of the fiber is modeled as a composite of extended molecules, in which the transfer of tensile stresses from molecule to matrix (other molecules) is poor. The case for poor intermolecular bonding is made by measuring torsional modulus of fibers both before and after heat treatment. The torsional modulus is small and invariant with heat treatment. Increasing the molecular length by solid state polymerization causes the fiber strength to increase.

Synthetic work was directed towards ascertaining whether chain ends are clustered fibers or not. Solid state NMR was identified as the best technique for obtaining this sort of information. Carbon-13 enriched p-hydroxybenzoic acid (HBA) was prepared using the following sequence: p-bromoanisole was reacted with magnesium in dry ethyl ether to form the Grignard reagent. The Grignard reagent was reacted with C-13 enriched carbon dioxide to form C-13 enriched HBA after acid hydrolysis. The C-13 label was therefore placed on the carboxylic carbon. Carbon-13 enriched 2-hydroxy-6-napthoic acid (HNA) was prepared using the following sequence: 2-bromo-6-methoxynapthalene was reacted with magnesium in dry tetrahydrofuran to form the corresponding Grignard reagent. The Grignard reagent was reacted with C-13 enriched carbon dioxide to form C-13 enriched HNA after acid hydrolysis. The C-13 label was therefore placed on the carboxylic carbon. Plans for the next few weeks include the preparation of the acetylated HBA and HNA monomers by reacting HBA and HNA with C-13 enriched acetyl chloride and melt polymerization of the acetylated monomers. We have sufficient quantity of monomer to produce at least 15g of polymer, which is what is required to melt spin the polymer into fibers. Fibers will then be analyzed using (COSY) solid state NMR.

PART II - TECHNICAL INFORMATION

Presentations scheduled:

1. **S.B. Warner** and J. Lee, "Heat Treatment of Thermotropic Copolyesters", Fiber Society Fall Meeting, Oct. 1993, Ithaca NY.
2. **J. Lee** and S.B. Warner, "Heat Treatment of Thermotropic Copolyesters" SPE Spring Meeting, May 1993, San Francisco, CA.

Publications submitted:

1. S.B. Warner and J. Lee, "Towards Understanding the Increase in Strength with Heat Treatment of Thermotropic Copolyesters", J. Poly Sci.: Pol. Physics, submitted in Sept. 1993.
2. J. Lee, "Understanding the Tenacity Increase with Heat Treatment of Thermotropic Copolyester Based on Oxybenzoate and Oxynapthoate", MS Thesis, accepted April 1993by the faculty of the School of Textile and Fiber Engineering at GA Tech.

There will be more publications and presentations whereupon the chemical aspects are completed.